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**(54) Title:** PROCESS FOR PREPARING A SPINNABLE, ISOTROPIC CELLULOSE SOLUTION

**(57) Abstract**

The invention pertains to a process for preparing a spinnable, isotropic solution containing 94-100 wt.% of the constituents cellulose, phosphoric acid and/or its anhydrides, and water, which solution is obtained by dissolving cellulose in a phosphoric acid-containing solvent, with the solvent containing 68-85 wt.% of phosphorus pentoxide, calculated on the overall quantity of water and phosphoric acid in the solvent. The solution can be used to make (hollow) fibres, membranes, non-wovens, films, and for other known applications of cellulose solutions.

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# PROCESS FOR PREPARING A SPINNABLE, ISOTROPIC CELLULOSE SOLUTION

The invention pertains to a process for preparing a spinnable, isotropic solution containing 94-100 wt.% of the constituents cellulose, phosphoric acid and/or its anhydrides, and water, which solution is obtained by dissolving cellulose in a phosphoric acid-containing solvent.

Such a process is known from GB patent publication 263 810, which describes the dissolution of linters cellulose in 85-90% $H_3PO_4$. The dissolution of cellulose can be facilitated by adding other reagents, such as glacial acetic acid and ethanol or homologues thereof. The overall time needed to obtain a homogeneous solution amounts to several hours. The solution can be used, e.g., for spinning artificial silk.

The process is also known from SU 1348396 and SU 1397456. In these publications various examples are provided of the dissolution of cellulose in 80-85% $H_3PO_4$. These publications show that the dissolving process takes up several hours (or a multiple thereof) and that during the process there may be a substantial decrease of the degree of polymerisation (DP) of the cellulose. The solutions can be used to make fibres or films.

Surprisingly, a simple process has now been found by means of which a homogeneous, spinnable, isotropic cellulose solution can be obtained.
The invention consists in that using the already known process cellulose is dissolved in a solvent containing 68-85 wt.% of phosphorus pentoxide, calculated on the overall quantity of water and phosphoric acid in the solvent.

A solution is considered to be isotropic when in a state of rest at room temperature it is not birefringent.
A spinnable solution is a solution which is suitable for being converted into fibres or filaments through extrusion, coagulation, and winding.

The term phosphoric acid in this patent application refers to all inorganic acids of phosphorus and their mixtures. Orthophosphoric acid is the acid of pentavalent phosphorus, i.e. $H_3PO_4$. Its anhydrous equivalent, i.e. the anhydride, is phosphorus pentoxide ($P_2O_5$). In addition to orthophosphoric acid and phosphorus pentoxide there is, depending on the quantity of water in the system, a series of acids of pentavalent phosphorus with a water-binding capacity in between those of phosphorus pentoxide and orthophosphoric acid, such as polyphosphoric acid ($H_6P_4O_{13}$, PPA).

The phosphorus content of the solvent is determined by converting the quantity by weight of phosphoric acid in the solvent into the equivalent quantity by weight of the accompanying anhydride and residual water. Thus converted, orthophosphoric acid is composed of 72,4 wt.% of phosphorus pentoxide and residual water, and $H_6P_4O_{13}$ is composed of 84 wt.% of phosphorus pentoxide and residual water.
The weight percentage of phosphorus pentoxide in the solvent is calculated by starting from the overall quantity by weight of phosphoric acid including its anhydrides and the total quantity of water in the solvent, converting the acids into phosphorus pentoxide and water, and calculating the percentage of said overall quantity by weight made up by phosphorus pentoxide.
In this description water derived from cellulose or from substances which are part of the other constituents and water which is added to obtain the solution are not included in the calculation of the concentration of phosphorus pentoxide in the solvent.

In order to effect more rapid dissolution of the cellulose, the solvent preferably contains 72-80 wt.% of phosphorus pentoxide.

The weight percentage of phosphorus pentoxide in the solution is calculated by starting from the overall quantity by weight of phosphoric acid including its anhydrides and the total quantity of water in the solution, converting the acids into phosphorus pentoxide and water, and calculating which percentage of said overall quantity by weight is made up by phosphorus pentoxide. For that reason in this description water derived from cellulose or from substances which are part of the other constituents and water which is added to obtain the solution are included in the calculation of the concentration of phosphorus pentoxide in the solution.

The weight percentage of cellulose in the solution is calculated by starting from the overall quantity by weight of all constituents in the solution.

Cellulose derivatised with phosphoric acid is included among the constituents making up 94-100 wt.% of the solution.
In the case of cellulose derivatised with phosphoric acid the percentages by weight of cellulose in the solution listed in this patent specification refer to quantities calculated back on the cellulose. This applies in analogous fashion to the quantities of phosphorus mentioned in this specification.

In addition to water, phosphoric acid and/or its anhydrides, and cellulose and/or reaction products of phosphoric acid and cellulose, other substances may be present in the solution.
The solution can be prepared by mixing constituents classifiable into four groups: cellulose, water, phosphoric acid including its anhydrides, and other constituents. The "other constituents" may be substances which benefit the

processability of the cellulose solution, solvents other than phosphoric acid, or adjuvants (additives), e.g., to counter cellulose decomposition as much as possible, or dyes and the like.

Preferably, the solution is composed of 96-100 wt.% of the constituents cellulose, phosphoric acid and/or its anhydrides, and water.
Preferably, no solvents other than phosphoric acid are employed, and adjuvants or additives are present only in amounts of 0 to 4 wt.%, calculated on the overall quantity by weight of the solution. More favoured still is a solution containing the lowest possible quantity of substances other than the constituents cellulose, phosphoric acid and/or its anhydrides, and water, i.e., with from 0 to 1 wt.% of additives.

Spinnable, isotropic solutions according to the invention can be obtained when the solution contains less than 20 wt.% of cellulose. It was found that by using the process according to the invention spinnable, isotropic cellulose solutions can be obtained where there is a clear connection between the cellulose concentration in the solution and the weight percentage of phosphorus pentoxide in the solution.
For instance, it was found that a spinnable, isotropic solution having a cellulose concentration of 4,8 wt.% can be obtained when the solution contains 58-75 wt.% of phosphorus pentoxide. A spinnable, isotropic solution having a cellulose concentration of 7,6 wt.% can be obtained when the solution contains 59-71 wt.% of phosphorus pentoxide. A spinnable, isotropic solution having a cellulose concentration of 11,4 wt.% can be obtained when the solution contains 61-69 wt.% of phosphorus pentoxide. A spinnable, isotropic solution having a cellulose concentration of 17,1 wt.% can be obtained when the solution contains 63-65 wt.% of phosphorus pentoxide.

As described in non-prepublished patent application WO 96/06208 in the name of Applicant, anisotropy may be observed in solutions obtained by dissolving cellulose in a solvent containing 65-80 wt.% of phosphorus pentoxide.

It has now been found that the anisotropic character of a solution containing less than 20 wt.% of cellulose depends, int. al., on the concentration of phosphorus pentoxide in the solution.

Thus it was found that an anisotropic solution having a cellulose concentration of 7,6 wt.% can be obtained when the solution contains 71-75 wt.% of phosphorus pentoxide. An anisotropic solution having a cellulose concentration of 11,4 wt.% can be obtained when the solution contains 69-76 wt.% of phosphorus pentoxide. An anisotropic solution having a cellulose concentration of 17,1 wt.% can be obtained when the solution contains 65-79 wt.% of phosphorus pentoxide.

Spinnable, isotropic solutions according to the present invention can be obtained by adding cellulose to a solvent containing 68-85 wt.% of phosphorus pentoxide in an appropriate mixing and/or kneading apparatus. In a favourable embodiment of the process according to the present invention, extra water is added to the solvent or the mixture formed by the cellulose and the solvent before, during or after the combination of the cellulose with the solvent. The extra water can be added in combination with other components, e.g., as water present in an other solvent, e.g., by the addition of extra phosphoric acid.

It was found that prior to the addition of cellulose and/or other components such as extra water, the solvent should be a homogeneous mixture of phosphoric acid and any other components which are present in the solvent. Such homogeneous mixture can be obtained, e.g., by mixing all components of the solvent at elevated temperature and keeping the solvent heated for

some time. Isotropic spinnable solutions having a cellulose concentration of 7 to 20 wt.% can only be obtained if extra water is added to the solvent or the mixture formed by the cellulose and the solvent just before, during or after the combination of the cellulose with the solvent.

It was further found that isotropic spinnable solutions having a cellulose concentration of 7 to 20 wt.% according to the present invention can be obtained from anisotropic cellulose solutions in the manner described in non-prepublished patent application WO 96/06208 in the name of Applicant, by reducing the phosphorus pentoxide content in the solution, e.g., by adding water to the anisotropic solutions.

As was described in non-prepublished patent application WO 96/06208, the dissolution of cellulose in a solvent containing mainly phosphoric acid is hindered/slowed down by the formation of an impermeable coating on the outside of the cellulose. In WO 96/06208 various ways of solving this problem are mentioned, such as rapidly and thoroughly mixing the cellulose and the solvent or the use of powdered cellulose or small cellulose chips.
It was found that this problem occurs not only in the preparation of anisotropic cellulose solutions (which have a comparatively high cellulose concentration in the solution), but also in the preparation of isotropic cellulose solutions. The potential answers to this problem put forward in WO 96/06208 were found to be suitable for use also when preparing isotropic solutions.

Preferably, the cellulose and the phosphoric acid-containing solvent are combined in an apparatus in which there can be intensive mixing in of one or more added constituents as a result of the shearing forces generated by mixing and kneading members in the apparatus, e.g., in a high-shear mixer. Examples of high-shear mixers such as are known to the skilled person

include a Linden-Z kneader, an IKA-duplex kneader, a Conterna kneader or a twin-screw extruder.

After the phosphoric acid-containing solvent and the cellulose have been combined in a mixing and kneading apparatus, the cellulose and the solvent are mixed and the cellulose dissolves. The degree of mixing should be such as will not slow the cellulose dissolution down too much through the formation of an impermeable coating on the outside of the cellulose. The dissolution of the cellulose can be slowed down by lowering the temperature. In one favoured process according to the invention, the cellulose and the solvent are combined in the apparatus, with the temperature in the section of the apparatus where the combination of the cellulose and the solvent takes place being less than 45°C, preferably in the range of 5 to 20°C. In another advantageous embodiment the solvent prior to being combined with the cellulose is cooled such that the temperature is less than 25°C. The cooling preferably takes place in such a way, e.g., by means of chilling, that there is no crystallisation of the solvent. Alternatively, solvent crystallisation can be prevented by rapid combination of the cellulose and the solvent.

In a favourable process according to the invention the construction of the apparatus is such that during the mixing and kneading the starting products and the formed solution are carried from a passage in the apparatus where the solvent and the cellulose are combined to a passage where the solution leaves the apparatus. Examples of such apparatus include a LIST-mixer, a twin-screw extruder, an IKA-Z kneader, and a Conterna kneader.

In such an apparatus different zones can be distinguished in the direction in which the products present in the apparatus are conveyed. Mixing of the supplied cellulose with the solvent and diminution will take place chiefly in the

first zone. In a following zone the dissolution of the cellulose will play a major part as well. A subsequent zone will mostly hold the prepared solution, which will be further homogenised and mixed with the not yet dissolved cellulose. If so desired, the solution can also be degassed.

In such an apparatus the cellulose dissolution and the properties of the prepared solution can be influenced by the temperature selected for the different zones.

By selecting a temperature in the first zone of less than 30°C, preferably in the range of 5 to 20°C, the dissolution of the cellulose can be slowed down. By increasing the temperature, e.g., in a subsequent zone, the cellulose dissolution is accelerated. It should be noted here that the dissolution of the cellulose and the combination of the solvent and the cellulose may be attended with the release of heat.

The DP of the cellulose solution can be controlled by selecting the temperature and the residence time in the zone of the mixing and kneading apparatus where chiefly cellulose in solution is present. As a general rule, the higher the temperature and the longer the residence time at this temperature are, the more the DP of the cellulose will be reduced. Furthermore, the DP of the starting material may have an effect on the DP reduction at a particular temperature and residence time.

Since the heat transfer between the products in the apparatus and the apparatus itself usually does not proceed in an ideal manner, differences in temperature can arise between the products in the apparatus and the apparatus itself.

The apparatus can also have a zone where the prepared solution is degassed, e.g., by being passed through a zone of reduced pressure. In this zone or in a

separate zone water or other constituents can be extracted from the prepared solution or added to it.

The prepared solution can be filtered in the apparatus or on leaving it to remove any minute undissolved particles from the solution.
The obtained solution is high-viscous. It can be used directly, but can also be stored for some time at low temperature, say, between -20 and 10°C. As a general rule, the longer the storage time desired for the solution, the lower the preferred temperature selected will be.
It should be noted that the obtained solution may solidify, e.g., by crystallising, if it is stored at a lower temperature for some time. Heating the formed solidified mass will again give a high-viscous solution.

By means of the above-described preparative process cellulose solutions with a controlled reduction of the cellulose DP can be made in a short period of time. For instance, it was found that a cellulose solution can be made from cellulose chips and a solvent containing phosphoric acid within 15 minutes and even in less time still. This period can be reduced further yet by selecting a higher temperature at which to prepare the solution.

For the preparation of the solution according to the invention use may be made of every available type of cellulose, e.g., Arbocell BER 600/30, Arbocell L 600/30, Buckeye V5, Buckeye V60, Buckeye V65, Viscokraft, and Eucalyptus cellulose, all types known to the skilled person. Cellulose can be supplied in a wide range of forms, including sheets, strips, scraps, chips or powder. The form in which the cellulose can be supplied is restricted by its introduction into the mixing and kneading apparatus. When the cellulose used is in such a form that it cannot be introduced into the apparatus, it has to be

made smaller outside the apparatus in a known manner, e.g., with the aid of a hammer mill or a shredder.

When a mixture of different phosphoric acids is employed to obtain a solvent having the desired quantity of acid converted into anhydride, it is preferred to heat the acids after they have been mixed to a temperature in the range of 30 to 80°C and to keep the solvent heated for ½-12 hours. In some cases other times and/or temperatures are desired, depending on the acids employed. For instance, a very homogeneous solution without irregularities is obtainable if use is made of a solvent obtained by melting orthophosphoric acid at a temperature in the range of about 40 to 60°C, adding the desired quantity of polyphosphoric acid to it, and then mixing the whole and cooling it down to about 20°C.

According to one suitable method, the solvent is left to stand for some time, say, from 30 minutes to several hours, at a temperature between 30 and 70°C, prior to being combined with the cellulose.
According to another highly suitable method, there is intensive stirring to do away with any local variations in low and high acid concentrations, and cellulose is added, optionally in the presence of small quantities of adjuvants or other constituents. As was described above, before, during or after the cellulose addition also extra water can be added to the solvent or the prepared mixture of cellulose and solvent.
Preferably, the solvent does not crystallise during the preparation.

In addition to water, phosphoric acid and/or its anhydrides, and cellulose and/or reaction products of phosphoric acid and cellulose, other constituents may be present in the solution.

These constituents may be added to the solvent prior to its combination with the cellulose. Alternatively, the other constituents may be added to the cellulose prior to its combination with the solvent. Furthermore, the other constituents may be added when the solvent and the cellulose are combined. And, of course, it is possible to add the other constituents after the solvent and the cellulose have been combined.

It was found that when the process according to the invention is employed, the solution contains at least 0,02 wt.% of phosphorus bound to the cellulose.
It was also found that by adding a small quantity of water to the solvent immediately before, simultaneous with, or shortly after the addition of the cellulose, a solution with a low content of cellulose-bound phosphorus is obtainable.
The temperature at which the solution is prepared and stored was found to affect the content of cellulose-bound phosphorus. As a general rule, a higher temperature during the preparation and/or storage will give a higher content of cellulose-bound phosphorus.
It was further found that the concentration of phosphorus pentoxide in the solvent has an effect on the content of cellulose-bound phosphorus. As a general rule, a higher concentration of phosphorus pentoxide in the solvent will give a higher content of cellulose-bound phosphorus.

The cellulose to be used preferably has an α-content of more than 90%, more particularly of more than 95%. For spinning good fibres from the solutions it is recommended to use so-called dissolving pulp with a high α-content, e.g., such as is generally employed in the manufacture of fibres for industrial and textile applications. Examples of suitable types of cellulose include Alphacell C-100, Arbocell BER 600/30, Buckeye V65 , Buckeye V5, Buckeye Cotton Linters, and Viscokraft. As determined by the procedure disclosed hereinafter

in this patent specification, the cellulose DP advantageously is in the range of 250 to 6000, preferably in the range of 500 to 5000. As a general rule, the spinnability of the solution is improved as cellulose with a higher DP is used in the preparation of the solution.

As is well-known to the skilled person, there will be a DP reduction during the dissolution of the cellulose. In consequence, the cellulose DP in the solution will be lower than the DP of the starting product.

Cellulose in the commercially available form generally contains some water (about 5 wt.%) and can be used as such without any objection. Of course, it is also possible to use dried cellulose, but this is not essential.

The invention further pertains to isotropic, spinnable, cellulose solutions, which can be obtained in a particularly advantageous manner using the above-described process. This holds especially for isotropic, spinnable solutions having a cellulose concentration in the range of 5 to 20 wt.%, more preferably in the range 10 to 20 wt.% and an phosphorus pentoxide content in the range of 60 to 71 wt.%, more preferably 63 to 71 wt.%, and for isotropic solutions having a cellulose concentration of less than 8 wt.% and a phosphorus pentoxide content in the range of 60 to 80 wt.%, more preferably 71 to 80 wt.%.

The isotropic cellulose solution can be put to various uses. For instance, the solution can be used in the manufacture of (hollow) fibres, membranes, non-wovens, films, and for other known applications of cellulose-containing solutions. In addition, the solution can be used to make cellulose derivatives.

**Measuring methods**

Determination of isotropy/anisotropy

Visual determination of the isotropy or anisotropy was performed with the aid of a polarisation microscope (Leitz Orthoplan-Pol (100x)). To this end about 100 mg of the solution to be defined were arranged between two slides and placed on a Mettler FP 82 hot-stage plate, after which the heating was switched on and the specimen heated at a rate of about 5°C/min. In the transition from anisotropic to isotropic, i.e., from coloured (birefringent) to black, the temperature is read off at virtual black. The transition temperature is indicated as $T_{ni}$.

The visual assessment during the phase transition was compared with an intensity measurement using a photosensitive cell mounted on the microscope. For this intensity measurement a specimen of 10-30 µm was arranged on a slide such that no colours were visible when crossed polarisers were employed. Heating was carried out as described above. The photosensitive cell, connected to a recorder, was used to write the intensity as a function of time. Above a certain temperature (differing for the different solutions) there was a linear decrease of the intensity. Extrapolation of this line to an intensity of 0 gave the $T_{ni}$. In all cases, the value found proved a good match for the value found by the above-mentioned method.

The solutions according to the invention are isotropic at room temperature. This means that $T_{ni}$ will be less than 25°C. However, there is a possibility that the solutions will not display any isotropy/anisotropy transition.

Determination of DP

The degree of polymerisation (DP) of the cellulose was determined with the aid of an Ubbelohde type 1 (k=0,01). To this end the cellulose specimens to be measured were dried *in vacuo* for 16 hours at 50°C after neutralisation, or the

amount of water in the copper II ethylene diamine/water mixture was corrected to take into account the water in the cellulose. In this way an 0,3 wt.% of cellulose-containing solution was made using a copper II ethylene diamine/water mixture (1/1).

On the resulting solution the viscosity ratio (visc. rat. or $\eta_{rel}$) was determined, and from this the limiting viscosity ($\eta$) was determined in accordance with the formula:

$$[\eta] = \frac{\text{visc.rat} - 1}{c + (k \times c \times (\text{visc.rat.} - 1))} \times 100$$

wherein c = cellulose concentration of the solution (g/dl) and

k = constant = 0,25

From this formula the degree of polymerisation DP was determined as follows:

$$DP = \frac{[\eta]}{0{,}42} \text{ (for } [\eta] < 450\ \text{ml/g), or}$$

$$DP^{0{,}76} = \frac{[\eta]}{2{,}29} \text{ (for } [\eta] > 450\ \text{ml/g)}$$

Determining the DP of the cellulose in the solution proceeded as described above after the following treatment:

20 g of the solution were charged to a Waring Blender (1 litre), 400 ml of water were added, and the whole was then mixed at the highest setting for 10 minutes. The resulting mixture was transferred to a sieve and washed thoroughly with water. Finally, there was neutralisation with a 2%-$NaHCO_3$ solution for several minutes and after-washing with water to a pH of about 7. The DP of the resulting product was determined as described above, starting from the preparation of the copper II ethylene diamine/water/cellulose solution.

Determination of phosphorus content

The quantity of phosphorus bound to the cellulose in the solution, or in a cellulose product made using said solution, can be determined by 300 mg of cellulose solution, which solution has been coagulated and, after thorough washing for 16 hours at 50°C, dried *in vacuo* and then stored in a sealed sampling vessel, being combined in a decomposition flask with 5 ml of concentrated sulphuric acid and 0,5 ml of an Yttrium solution containing 1000 mg/l of Yttrium. The cellulose is carbonised with heating. After carbonisation hydrogen peroxide is added to the mixture in portions of 2 ml, until a clear solution is obtained. After cooling the solution is made up with water to a volume of 50 ml. ICP-ES (Inductive Coupled Plasma - Emission Spectrometry) is used to measure, by means of a phosphorus calibration line determined using reference samples containing 100, 40, 20, and 0 mg/l of phosphorus, respectively, the phosphorus content in the solution to be measured with the aid of the following equation:

phosphorus content (%) = $(P_{conc}(mg/l)*50)/(C_w(mg)*10)$

wherein: $P_{conc}$ = the phosphorus concentration in the solution to be measured and

$C_w$ = the weighed out quantity of coagulated and washed cellulose.

Yttrium is added as internal standard to correct the solutions' viscosity variations. The phosphorus content is measured at a wavelength of 213,6 nm, the internal standard is measured at a wavelength of 224,6 nm.

The invention will be elucidated with reference to the examples below.

Unless specified otherwise, the following starting materials with accompanying specifications were used to make the solutions in the examples.

| Material | Manufacturer and product code | $P_2O_5$ content [%] |
|---|---|---|
| $P_2O_5$ | J.T. Baker, 0193 | 98 |
| $H_3PO_4$ | La Fonte Electrique SA, Bex Suisse crystallised, >99% (98,8% anal.) | 71,2 |
| $H_4P_2O_7$ | Fluke Chemika, 83210, 97%, (98,8% anal.) | 78,8 |
| PPA* | Merck, 85% min. | 84 |
| $H_2O$ | demineralised | -- |

*PPA = polyphosphoric acid

**Examples**

Example 1

15,4 g of Buckeye Cotton Linters (DP=5900) were dissolved at 20°C in a solvent containing phosphorus pentoxide. This solvent was obtained by mixing and kneading 238,3 g of ortho-phosphoric acid and 54,7 g of polyphosphoric acid for 30 minutes at 50°C. 10 minutes after the addition of the cellulose with mixing at 20°C a viscous isotropic solution was obtained which contained undissolved particles still discernible by microscope. After 72 minutes of mixing at 20°C a homogeneous, spinnable, isotropic solution was obtained. The DP of the cellulose in solution was 850.

In this way an isotropic, spinnable solution containing 73,4 wt.% of phosphorus pentoxide and 4,7 wt.% of cellulose was obtained, starting from a solvent containing 73,6 wt.% of phosphorus pentoxide.

Example 2

13,1 g of powdered cellulose (DP=2300) were dissolved at 20°C in a solvent containing phosphorus pentoxide. This solvent was obtained by mixing and

kneading 199,2 g of ortho-phosphoric acid and 48,8 g of polyphosphoric acid for 40 minutes at 50°C. 27 minutes after the addition of cellulose with mixing at 20°C a viscous isotropic solution was obtained which contained undissolved particles still discernible by microscope. After 67 minutes of mixing at 20°C a homogeneous, spinnable, isotropic solution was obtained.

In this manner an isotropic, spinnable solution containing 73,5 wt.% of phosphorus pentoxide and 4,8 wt.% of cellulose was obtained, starting from a solvent containing 73,7 wt.% of phosphorus pentoxide.

Example 3

In a kneader a solvent was prepared at 45°C by mixing and kneading 199,8 g of ortho-phosphoric acid and 54,8 g of polyphosphoric acid for 30 minutes. 60,7 g of the solvent was taken from the kneader for other experiments and the remainder cooled to 18°C. To this were added 32,8 g of water and, after 1 minute of kneading and mixing, 49,8 g of powdered cellulose (DP=700).

After 60 minutes mixing and kneading at 18°C, the cellulose had dissolved completely and a homogeneous, spinnable, isotropic solution was obtained.

In this manner an isotropic, spinnable solution containing 62,6 wt.% of phosphorus pentoxide and 17,1 wt.% of cellulose was obtained, starting from a solvent containing 74,0 wt.% of phosphorus pentoxide.

Example 4

In a kneader a solvent was prepared at 50°C by mixing and kneading 122,7 g of ortho-phosphoric acid and 34,0 g of polyphosphoric acid for 45 minutes. The solvent was cooled to 18°C. To it were added 31,0 g of water and, after 1 minute of kneading and mixing, 25,6 g of powdered cellulose (DP=700).

After 78 minutes mixing and kneading at 18°C, the cellulose had dissolved almost completely and a spinnable, isotropic solution was obtained.

In this manner an isotropic, spinnable solution containing 61,4 wt.% of phosphorus pentoxide and 11,4 wt.% of cellulose was obtained, starting from a solvent containing 74,0 wt.% of phosphorus pentoxide.

Example 5

To the contents of a Linden kneader, 70,4 parts by weight of polyphosphoric acid (84 wt.% of phosphorus pentoxide), there were added at 18°C 17,6 parts by weight of water and 12 parts by weight of powdered cellulose (DP=700). The contents of the kneader were vigorously mixed and kneaded at 18°C. After 30 minutes a homogeneous, spinnable, isotropic cellulose solution was obtained.

In this manner an isotropic, spinnable solution containing 66,7 wt.% of phosphorus pentoxide and 11,4 wt.% of cellulose was obtained, starting from a solvent containing 84,0 wt.% of phosphorus pentoxide.

Example 6

In a kneader a solvent was prepared at 45°C by mixing and kneading 72,2 g of ortho-phosphoric acid and 16,6 g polyphosphoric acid for 45 minutes. Then the solvent was cooled to 10°C. To this were added 16 g of cellulose powder (DP=700). After 10 minutes kneading and mixing at 20 °C the cellulose was dissolved completely. To this homogeneous solution 293,4 g of $H_3PO_4$ (80%) were added.

After mixing during several hours a homogeneous, spinnable, isotropic cellulose solution was obtained containing 61,7 wt.% of phosphorus pentoxide and 3,8 wt.% of cellulose, starting from a solvent containing 74,5 wt.% of phosphorus pentoxide.

Example 7

In a kneader a solvent was prepared at 45°C by mixing and kneading 78,3 parts by weight of ortho-phosphoric acid and 21,7 parts by weight of polyphosphoric acid for 45 minutes. From this solvent 235,1 g were transferred to a kneader and cooled to 3 °C. To this were added 62,1 g of cellulose powder (DP=700). 7 minutes later the cellulose were completely and homogeneously dissolved. The temperature were 16°C. Under constant kneading and mixing at 20 °C to this were added during 25 minutes 48 g water.

A homogeneous, spinnable, isotropic cellulose solution was obtained containing 60,8 wt.% of phosphorus pentoxide and 17,1 wt.% of cellulose, starting from a solvent containing 74,0 wt.% of phosphorus pentoxide.

Example 8

A solvent was prepared by mixing and heating orthophosphoric acid and polyphosphoric acid in such a ratio that a solvent with a concentration of 74.5 wt.% $P_2O_5$ was obtained. 60.6 g of powdered cellulose (DP=700), which contained 4 wt.% equilibrium moisture, was added to 276 g of the solvent in an IKA-Duplex kneader. The components were kneaded at a temperature below 20 °C and a homogeneous, shiny, fiber-formimg solution was obtained. To this solution water was added stepwise until a isotropic spinnable solution was obtained, which contained 15.1 wt.% cellulose and 63.4 wt.% $P_2O_5$. The solution had a clearing temperature ($T_{ni}$) of 10°C.

Example 9

In a Linden-Z kneader with extruder discharge a solvent was prepared at 50°C by mixing and kneading 14890 g of ortho-phosphoric acid and 4110 g of polyphosphoric acid for 45 minutes. The solvent was cooled to 12°C. To it were added 1650 cellulose (Alphacell-C-100, DP=2300). Kneading was

continued for 60 minutes, the last 50 of them with degassing. During the kneading of the solution the temperature was kept at 20 °C.
In this manner an isotropic, spinnable solution containing 73.8 wt.% of phosphorus pentoxide and 7,6 wt.% of cellulose was obtained, starting from a solvent containing 74,1 wt.% of phosphorus pentoxide.
This solution was extruded at 40°C through a spinneret having 375 capillaries each with a diameter of 65 µm. The extruded solution was passed through an air gap and coagulated in a bath filled with acetone of about 35°C. After coagulation the multifilament yarn formed was washed with water and neutralised with a 2,5 wt.% $Na_2CO_3 \cdot 10H_2O$ solution in water. The yarn was then dried under very low tension.
Several experiments were carried out with different draw ratios in the air gap, the draw ratio being defined as the throughput rate in the coagulation bath divided by the rate at which the solution was extruded from the capillaries.
The mechanical properties of the resulting yarns were measured. The data is listed in Table 1.

Table 1

| | DR | Lin. den. [dtex] | BT [mN/tex] | EaB [%] | IM [N/tex] | FM [N/tex] | BTo [J/g] |
|---|---|---|---|---|---|---|---|
| 9a | 0,6 | 3320 | 180 | 17,4 | 3,5 | 1,6 | 18,6 |
| 9b | 0,9 | 2390 | 270 | 11,5 | 5,7 | 3,0 | 17,0 |
| 9c | 1,1 | 1770 | 310 | 9,5 | 7,6 | 4,2 | 16,1 |
| 9d | 1,5 | 1370 | 380 | 8,4 | 9,2 | 6,0 | 16,6 |

wherein DR = draw ratio, BT = Breaking tenacity, EaB = Elongation at break, IM = Initial modulus, FM = Final modulus, and Bto = Breaking toughness.

Comparative example

In a kneader a solvent was prepared at 45°C by mixing and kneading for 60 minutes 84 parts by weight of polyphosphoric acid (84 wt.% of phosphorus pentoxide) and 16 parts by weight of water. The obtained homogeneous solution was cooled to 18°C and 9 parts by weight of powdered cellulose were added. The contents of the kneader were mixed and kneaded at for 60 minutes. Even after 60 minutes a mixing and kneading action it was not possible to obtain a homogeneous, spinnable, isotropic cellulose solution. The obtained mixture was of low viscosity with many undissolved cellulose parts.

This comparative example shows that it is not possible to obtain an isotropic, spinnable cellulose solution containing 70,2 wt.% of phosphorus pentoxide and 7,8 wt.% of cellulose, starting from a solvent containing 70,5 wt.% of phosphorus pentoxide without the addition of extra water.

**Claims**

1. A process for preparing an isotropic, spinnable solution containing 94-100 wt.% of the constituents cellulose, phosphoric acid and/or its anhydrides, and water, which solution is obtained by dissolving cellulose in a phosphoric acid-containing solvent, characterised in that the solvent contains 68-85 wt.% of phosphorus pentoxide, calculated on the overall quantity of water and phosphoric acid in the solvent.

2. A process according to claim 1, characterised in that cellulose is added to the solvent and that before, during or after the cellulose addition also water is added to the solvent or to the mixture containing the cellulose and the solvent.

3. A process according to claim 2, characterised in that the obtained solution contains 7 - 20 wt.% of cellulose.

4. A process according to claim 1 or 2, characterised in that after the dissolution of the cellulose an anisotropic cellulose solution is formed, to which anisotropic solution water is added.

5. A process according to any one of the preceding claims, characterised in that the solvent contains 72-80 wt.% of phosphorus pentoxide.

6. An isotropic, spinnable, cellulose solution containing 10-20 wt.% of cellulose and 60-71 wt.% of phosphorus pentoxide.

# INTERNATIONAL SEARCH REPORT

Inter onal Application No
PCT/EP 97/00460

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D01F2/02 D01F2/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D01F C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| P,X | WO 96 09356 A (MICHELIN RECH TECH) 28 March 1996<br>see example III.5 | 1-6 |
| P,X | WO 96 06208 A (AKZO NOBEL NV) 29 February 1996<br>cited in the application<br>see example 1 | 1-6 |
| A | NL 54 859 C (CELLULOSE PATENTS (INTERNATIONAL) LTD.) 15 July 1943<br>see the whole document | 1-6 |
| A | DE 714 434 C (JAN CORNELIS DE NOOIJ ET AL) 28 November 1941<br>see the whole document | 1-6 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+31-70) 340-3016 | Tarrida Torrell, J |

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International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | DATABASE WPI<br>Section Ch, Week 8822<br>Derwent Publications Ltd., London, GB;<br>Class A11, AN 88-153465<br>XP002015612<br>& SU 1 348 396 A (PHYS-CHEM PROBLEMS) , 30 October 1987<br>cited in the application<br>see abstract<br>--- | 1-6 |
| A | GB 263 810 A (BRITISH CELANESE LTD) 23 December 1926<br>cited in the application<br>see the whole document<br>----- | 1-6 |

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Information on patent family members

International Application No
PCT/EP 97/00460

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| DE 714434 C | | NONE | |
| GB 263810 A | | NONE | |